3.0 SAMPLING

This section presents guidelines for the collection, preservation, and transportation of waste samples and environmental samples. This field is still dynamic, so guidelines will change as more research is completed on the behavior of contaminants in samples. This section was compiled from a number of sources; the primary sources are listed at the end of each subsection.

Questions regarding any of the topics covered here should be directed to the contacts listed in Section 4.0, or the appropriate reference should be consulted.

3.1 SAMPLING PLANS

Sampling is generally the source of most errors in environmental measurement. Controlling sampling errors to acceptable levels requires attention to the steps described below. Whenever feasible, the sampling and analysis procedures should be defined in a sampling and analysis plan (SAP), Field Sampling Plan (FSP), or other plan. Such plans should be written after DQOs have been developed (Section 1).

3.1.1 What is the Problem?

Sampling will likely not be successful unless the project objectives have been determined in advance. Two common objectives for sampling are waste classification and site assessment. Waste classification typically involves sampling waste streams (e.g., drums and piles), while site assessment involves sampling air, water, soil, soil gas, or other media which may have been contaminated by hazardous materials.

3.1.1.1 Waste Classification.

Waste classification typically answers the question: Is this waste a hazardous waste? In such cases, samples should be representative of the waste stream. That is, the average properties of the samples generally should provide an acceptable estimate of the average properties of the entire waste stream. The definition of representative sample from Title 22 is one that has the average properties of the waste being sampled. While this is sometimes a worthwhile goal, it is rarely possible to obtain one real world sample of an industrial waste which has the average properties of the entire waste.

Waste sampling and analysis may also be done to answer the question: What is it? This is often the case for sampling inadequately labeled drums, carboys, or other containers. Because information obtained in the field (e.g. field analysis) may tentatively identify substances of concern, sampling plans may need to be modified as information becomes available. For example, if field screening indicates that a group of drums contains the same waste type, a stratified random sampling may be appropriate, as will be discussed below.

Waste generators are directed by Title 22 to comply with Chapter 9 of SW-846 for sampling and sample handling. EPA has drafted a stand-alone sampling guidance document entitled "RCRA Waste Sampling Draft Technical Guidance." (http://www.epa.gov/epaoswer/hazwaste/test/samp_guid.htm) This guidance was proposed as a replacement for the current sampling guidance version of Chapter Nine found in EPA publication SW-846. EPA is currently reviewing comments on the document and will release the document after it is revised. Until the completion of the Technical Guidance, Chapter Nine will remain the applicable guidance.

The American Society for Testing and Materials (ASTM) has published numerous standards and guides for sampling. The ASTM documents are available at engineering libraries and from ASTM.

Mailing address: ASTM
1916 Race Street
Philadelphia, PA 19103

Internet address: http://www.astm.org/

3.1.1.2 Site Assessment.

Sampling for site assessment may be quite different than sampling for waste characterization. The questions of interest may be: "What is the type and extent of contamination?" or "Has disposal of a hazardous waste occurred?" The Data Quality Objective process can produce an optimum sampling and analysis plan based on available resources. For more information, refer to EPA's "Methods for Evaluating the Attainment of Cleanup Standards. Volume 1: Soils and Solid Media," EPA 230/02-89-042.

3.1.1.3. "Clean Closure" Soil Sampling.

A particular problem in sampling is how to determine whether a site has been cleaned up to either a cleanup level or to a "background" level. The purpose in this case is generally to determine whether contamination on site is greater than the cleanup or background level. In order to prepare an adequate sampling plan, it is necessary to establish in advance what cleanup criteria will be used. If "background" is to be used, either data can be collected from control areas near the site or existing ambient levels can be used, e.g., USGS Geological Survey data on elemental levels in uncontaminated land. The control areas should be selected which are similar to the site in soil type and proximity to other sources of contamination, such as freeways. Caution must be used in using published data from the U.S. Geological Survey and the University of California, as these data can be too sparse to apply to specific sites. Further these data are of total soil element concentrations and not comparable to "TTLC" concentrations which are not total but partial acid digestions.

For addition information in determining whether site soil contamination is significantly greater than "background", refer to EPA's "Statistical Methods for Evaluating the Attainment of Cleanup Standards. Volume 3: Reference-Based Standards for Soils and Solid Media," EPA 230-R-94-004. This guidance presumes that site soils can be compared to soils of a similar type that are uncontaminated.

For additional information on cleaning up a site to predetermined "cleanup levels", refer to

EPA's "Methods for Evaluating the Attainment of Cleanup Standards. Volume 1: Soils and Solid Media," EPA 230/02-89-042. (http://www.clu-in.org/download/stats/vol1soils.pdf)

The sections below discuss the problems of determining the number of samples and evaluating the results.

3.1.1.4 Groundwater monitoring.

Groundwater monitoring requires careful specification of sampling and analytical methods. The purpose of such monitoring should be clearly established in a written plan well in advance of the sampling. The choice of sampling techniques, filtration techniques, analytical methods, and quality control samples will depend on the purpose of the sampling, as discussed in Section 3.2. For guidance on groundwater sampling and data interpretation, refer to "Methods for Evaluating the Attainment of Cleanup Standards. Volume 2: Ground Water," EPA 230-R-92-014.
(http://www.clu-in.org/download/stats/vol2gw.pdf)

3.1.1.5 Air Monitoring.

Typical purposes of air monitoring are: (1) to determine the magnitude of a source by comparing upwind and downwind concentrations, or (2) to determine the average concentration of some substance over a specified area and time interval.

3.1.2 Standard Operation Procedures (SOPs) for Sampling.

Examples of sampling SOPs can be found at website
http://www.epa.gov/region4/sesd/eabsop/eabsop.pdf.

3.1.3 Sampling Strategies.

Once the purpose of sampling has been established, the appropriate sampling strategy can be chosen. As mentioned above, references are available for choosing sampling strategies, depending on the purpose. This section will briefly describe the most common strategies, along with the implications for laboratory analysis.

3.1.3.1 Authoritative Sampling.

In authoritative (also called targeted or judgmental) sampling, the person collecting the sample decides on the sampling locations- generally to find the area of highest contamination. In a number of situations, this is the strategy of choice to determine whether disposal has occurred or to determine whether more extensive sampling is warranted. This strategy requires the fewest samples and provides the smallest number of measurements

below detection limits. This is usually the technique of choice to find "hot spots" or to find evidence of past disposal. This type of design can be very effective if the collector is familiar and knowledgeable about the site, and if goal of sampling is merely to establish that contamination may exceed some set criteria.

3.1.3.2 Random Sampling.

Random sampling allows statistical inferences to be made about an entire waste or other area. For example, one can calculate the mean and standard deviation for the concentration of a substance, plus a confidence interval which contains the true mean concentration, at a given level of confidence. Random sampling may be simple, stratified, or systematic. All three strategies for random sampling typically involve placing a grid over a map of the area to be sampled.

1) Simple Random Sampling

Using random sampling, the sampling and analysis of all samples should be identical so that bias is minimized. Simple random sampling can involve placing one grid over a map of the entire area and randomly choosing grid cells to sample. This method results in estimates of parameters (e.g., mean and standard deviation) for the entire area.

2) Stratified Random Sampling

The sampling and analytical procedures for stratified sampling are generally the same as for simple random sampling, although the evaluation of the data is different. In this strategy, the soil or solid waste (i.e., the "population") is divided into subregions (i.e., "strata") that are believed to be internally more homogeneous. Each subregion is randomly sampled. Means and variances for each subregion are calculated and used to calculate an overall mean and variance for the population. The statistical methods used to estimate the overall mean and variance presume that data are normally distributed. Examples include differentiating between highly contaminated (hot spots) and less contaminated areas or between surface, intermediate, and bottom layers of an impoundment.

3) Systematic Sampling

Systematic sampling involves the collection of samples at predetermined, regular, intervals; for example, samples taken at ten foot intervals along a line from an outfall. This technique is often used, but can result in biased results if there are periodic variations in the material to be sampled. Systematic sampling also minimizes the effect of spatially correlated data on estimate of sample variance.

3.1.3.3 Composite Sampling.

Compositing of samples is an effective way to reduce analysis costs. From a statistical point of view, compositing of samples loses information which would have been provided by the individual samples, but reduces the variability per composite sample. Compositing also, in effect, raises the analytical detection limit for the individual sub-samples because each sample is diluted by the other samples in the composite. The effective detection limit of each subsample is:

$$DL_S = DL_C \text{ X } n,$$

Where DL_S = Detection limit for each subsample,
DL_C = Detection limit for the composite sample,
n = Number of subsamples in the composite sample.

For example, if the detection limit for lead in a composite soil sample was 1 mg/kg (ppm) and each composite was made from 5 subsamples, then the effective detection limit for lead in each subsample is (1 mg/kg)(5) = 5 mg/kg (ppm).

Composite samples are sometimes preferred over individual samples in order to reduce analytical costs by reducing the number of samples. If the detection of hot spots is the sampling objective, then composite sampling can yield significant savings if the probability of exceeding an action level is less than 10%. One approach which has been successfully used is to prepare composites from portions of the original samples and archive the remainder of the original samples. The results of the composite samples can then be used to determine what analysis, if any, is needed on the archived samples. The holding times for the analytical methods should be considered with this strategy.

For additional information refer to ASTM standard D 6051-96 titled "Standard Guide for Composite Sampling and Field Subsampling for Environmental Waste Management Activities". This standard may be obtained from ASTM through their web site: http://www.astm.org.

3.1.3.4 Homogenizing and Splitting Samples.

Splitting samples is often necessary to provide samples to a defendant or responsible party, to send blind duplicate samples to the same lab, or to send split samples to a reference lab. Homogeneous material, such as water or fine grained soil, can be easily split in the field. Moderately heterogeneous material, such as coarse-grained soils, can generally be homogenized and split in the field using an additional container. The materials used for homogenization should be the same as the materials recommended for sample

containers in Section 3.6. The homogenization of soil samples prior to volatile organics analysis can result in significant losses, so co-located samples should be collected instead of split samples. Extremely heterogeneous material, such as mixtures of oil and water, may need to be split in a laboratory. If necessary, contact the lab which will be doing the compositing to obtain their standard procedure for sample splitting. Chain of custody must be maintained on the material from the initial point of collection, through sample splitting, to analysis. Chain of custody will be discussed further in Section 3.9. For additional information refer to ASTM standard D 6323 98 titled "Standard Guide for Laboratory Subsampling of Media Related to Waste Management Activities". This standard may be obtained from ASTM through their web site: http://www.astm.org.

3.1.4 Statistical Considerations.

In some sampling situations, statistical parameters must be considered before sampling. These include estimates of the mean (average) and variance, calculation of the appropriate number of samples, and selection of appropriate sampling locations. Detailed procedures for data analysis can be found in *Guidance for Data Assessment,* EPA QA/G-9.
Internet address: http://www.epa.gov/quality/qa_docs.html

Both the required number of samples to be collected and the final statistical analysis depend on the purpose of the sampling. In Case 1, below, which is relevant to waste classification, the average concentration of the results for randomly collected samples, is compared to a regulatory threshold, e.g., a Total Threshold Limit Concentration (TTLC) or Soluble Threshold Limit Concentration (STLC). The object of this sampling is to determine whether the average waste concentration is above the set threshold. Case 2, which describes Site Assessment, involves both random sampling, as described in Case 1, and authoritative sampling, which is not usually amenable to statistical analysis. In Case 3, which is relevant to Clean Closure as well as other activities, the average sample concentration is compared to the average concentration of background samples. In this case, there is statistical uncertainty or variability in both the sample and background concentration means.

In either statistical treatment, the tradeoffs in deciding the number of samples are 1) the amount of data and the corresponding confidence in results, versus 2) the costs and time for sampling and analysis. Chapters 9 and 10 of SW-846 and other references (e.g., EPA's Sampling Quality Assurance User's Guide or ASTM D4687 Standard Guide for General Planning of Waste Sampling) provide guidance on selecting the appropriate minimum number of samples when the cost of sampling and analysis is considered. The following approaches do not explicitly consider cost, but the chosen level of confidence will influence cost.

Example 1 - Waste Classification

Here are examples of DQOs for a generator's waste classification.

Step 1: State the Problem. To properly manage waste, the generator must classify a wastestream according to California hazardous waste regulations.

Step 2: Identify the Decision. If a waste exceeds any of the Hazardous waste criteria, it will be classified as a hazardous waste.

Step 3: Identify the Inputs to the Decision. The waste in question, a burn dump ash, is known to contain elements, especially copper and lead, which could render it hazardous. Data are needed for total metals, Waste Extraction Test (WET)-metals, Toxicity Characteristic Leaching Procedure (TCLP)-metals on an adequate number of samples.

Step 4. Define the Study Boundaries. The vertical and horizontal extent of the burn ash is determined from available data, and field observations.

Step 5. Develop a Decision Rule. If the mean total concentration exceeds a Total Threshold Limit Concentration (TTLC); or if the mean extractable concentration exceeds the respective Soluble Threshold Limit Concentration (STLC) or TCLP Limit, the waste will be classified hazardous.

Step 6. Specify Acceptable Limits on Decision Errors. Based on the guidance in the SW-846 Field Manual, an 80% confidence interval will be used for waste classification. If the mean concentration exceeds the lower 80% confidence interval of the mean, the waste will be judged hazardous. There is a 10% chance that the true mean is greater than the upper 80% confidence interval, i.e., there is a 10% chance of a false negative decision.

To compare the mean concentration with a regulatory limit, the Student's t-test is often used. This treatment assumes that the samples are independent of each other and the contaminant concentrations have a normal distribution. In environmental samples, these assumptions may not be met. As Student's t-test is not very sensitive to small deviations from normal distribution, often the t-test may still be used.

If, however, there is a substantial deviation from normality, the data may have to be transformed to approximate a normal distribution. The most common transformation with environmental data is a logarithmic transformation (usually the natural logarithm, ln). The references should be consulted for details on statistical tests with log-transformed data.

In order to determine whether the average contaminant concentration is above the regulatory threshold with a certain level of confidence, the required number of samples is given by equation 3-1.

$$n = \frac{t_{1-\alpha}^2 s^2}{\left(RT - \bar{x}\right)^2}$$ *Equation 3-1*

In which t = Student's t statistic at the desired confidence level, 1-α, s = the sample standard deviation, RT = the Regulatory Threshold, and $\bar{x}$ = the sample mean. For California hazardous waste criteria, the RT may be a Total Threshold Limit Concentration (TTLC), a Soluble Limit Threshold Limit Concentration (STLC), or an established background level.

SW-846 specifies that $t_{0.2}$ should be read from a two-tailed t table, as presented in Table 3.1-1. This is numerically equal to $t_{0.1}$ read from an one-tailed t table.

Table 3.1-1 Tabulated Values of Student's "t" for evaluating Solid Wastes

Degrees of freedom (n-1)[a]	Tabulated "T" value[b]
1	3.078
2	1.886
3	1.638
4	1.533
5	1.476
6	1.440
7	1.415
8	1.397
9	1.393
10	1.372
11	1.363
12	1.356
13	1.350
14	1.345
15	1.341
16	1.337
17	1.333
18	1.330
19	1.328
20	1.325
21	1.323
22	1.321
23	1.319
24	1.318
25	1.316
26	1.315
27	1.314
28	1.313
29	1.311
30	1.310
40	1.303
60	1.296
120	1.289

[a] Degree of Freedom (df) are equal to the number of samples (n) collected from a solid waste less one.
[b] Tabulated "t" values are for a two-tailed confidence interval and a probability of 0.20 (the same values are applicable to a one-tailed confidence interval and a probability of 0.10).

Since this approach requires some previous knowledge about the distribution of contaminants, it can best be carried out when preliminary sampling has been performed and the results used to calculate the number of samples for the second sampling. The mean and standard deviation are estimated from the preliminary sampling. The appropriate t statistic is found in the table and the resulting number of samples required to achieve that level of confidence is calculated. The value for t in the row corresponding to (n-1) degrees of freedom is chosen. Because the value of t depends upon the number of samples collected, an iterative approach can be used in which a number of samples is postulated, the appropriate t chosen, and the number of samples is calculated according to Equation 3-1. This is repeated until the calculated n is as close as possible to the postulated n which corresponds to the t value. The number of samples is always rounded up to the larger number when a fractional number results. Four samples are considered to be the minimum number for waste classification advised by EPA in SW-846.

Step 7. Optimize the Design for Obtaining Data. The number of needed samples can be calculated from equation 3-1. However, since the objective is to estimate the mean concentration, composite sampling (3.1.2.3) can be used to reduce the number of samples required for analysis. When the final sampling is conducted, a few additional samples should be collected because if the standard deviation of the samples is higher than the standard deviation of the preliminary samples, the required n will be higher. These additional samples may be archived and analyzed only as needed, if the holding times permit.

If the average contaminant concentration is above the regulatory threshold, the waste is to be considered hazardous. If the average concentration is below the regulatory threshold, the waste may still be considered hazardous if the regulatory threshold falls within the confidence interval of the average concentration. That confidence interval is calculated according to Equation 3-2:

$$Cl = \bar{x} \pm t_{0.2} s / \sqrt{n} \qquad \textit{Equation 3-2}$$

In which $t_{0.2}$ is obtained from the two-tailed t-table presented in Table 3.1-1, $\bar{x}$ is the mean of the sample concentrations, s is the standard deviation of the sample concentrations, and n is the number of samples.

Use of the Student's t-test assumes that the contaminants are normally distributed across the site. If this is not the case (determined through use of a goodness-of-fit test), the data can be transformed by scaling all of the data values. The most common transformations are obtained by taking the logarithm or square root of each concentration datum. The resulting transformed data may have a normal distribution even if the original data did not.

An alternative to the two sample t-test is a non-parametric test; EPA G-9 or another reference on nonparametric statistics should be consulted.

3.1.5 Elements of the Sampling Plan.

Before a sampling project is begun, a sampling plan should be drawn up. Elements which should be included in such a plan are:

I. Objective and scope of the sampling
   A. Brief description of site
   B. Background and objective of monitoring
   C. Personnel in charge of sampling

II. Sampling Overview
   A. Map of site with sampling locations
      - sampling strategies
      - types of samples to be collected
   B. Analyses to be performed (table)
      - aliquots (volumes/weights)
      - containers
      - preservatives
      - special handling
      - analytical methods to be used
   C. Monitoring well details (if wells included)
      - well depth
      - screened interval
      - casing diameter
      - previous depth to water measurement
      - dedicated pumping equipment
      - estimated purge and recovery time
   D. Sampling and shipping schedule

III. Presampling Procedures
   A. Safety survey
      - instruments and procedures
      - concentration limits for each level of protection
      - clothing and other protective equipment
   B. Well preparation (if wells included)
      - physical measurements (depth to water, etc.)
      - well purging (volume, method, disposal)
      - procedure for slowly recharging wells
   C. Field measurements (parameters, methods)

IV. Sample Collection
   A. Equipment and procedures
   B. Order of collection

V. QC Samples (types, numbers, procedures, locations)

VI. Decontamination
- A. Equipment (procedures, schedule)
- B. Personnel decontamination procedures

VII. Documentation
- A. Logbooks
  - required inclusions
  - assigned person
- B. Photographs

VIII. Chain of Custody requirements

IX. Labeling and packaging of samples

X. Transportation

Several of these elements can be used with only minor modifications for many different projects. Other elements may need to be written specifically for each project.

3.1.6 References.

1) U.S. EPA, "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846, 3d ed. SW-846 is available online at: http://www.epa.gov/epaoswer/hazwaste/test/main.htm

2) Gibbons, J. D., Nonparametric Methods for Quantitative Analysis (Second Edition), American Sciences Press, Columbus, Ohio, 1985.

3) Gilbert, Richard O., Statistical Methods for Environmental Pollution Monitoring, Van Nostrand Reinhold Co., New York, 1987.

4) Keith, Lawrence K., "Principles of Environmental Sampling," Environ Sci Technol, Vol 24, pp 610-617, May, 1990.

5) ASTM: D4687, Standard Guide for General Planning of Waste Sampling.

6) RCRA Waste Sampling Draft Technical Guidance, 2002 http://www.epa.gov/SW-846/samp_guid.htm

3.2 WATER SAMPLING.

3.2.1 Groundwater.

The following section briefly describes sample collection from groundwater monitoring wells and is not comprehensive. For further information, see Appendix B of Guidance Document, Monitoring Requirements for Permitted Hazardous Waste Facilities (GSU, 2001), Representative Sampling of Ground Water for Hazardous Substances (CALEPA, 1995), Practical Handbook of Ground-Water Monitoring (Nielsen, 1991), and Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures (Puls and Barcelona, 1996) the source for much of this section.

3.2.1.1. Detection of Organic Vapors in Well Headspace.

It may be necessary to monitor the air at and around the well head immediately upon opening the well using a direct reading instrument such as an organic vapor analyzer (OVA), photoionization detector (PID), and/or a combustible gas indicator (CGI) to determine the potential for fire, explosion, or other health and safety hazards. Detailed plans and acceptable limits should be included in the health and safety portion of the sampling plan.

3.2.1.2 Measurement of Static Water Level Elevation.

Routine measurement of static water level elevations are important to determine whether the predicted horizontal and vertical flow gradients have changed since last measured. Measurements should include the depth to standing water and often the depth to the bottom of the well casing. This information may be needed to calculate the volume of water to purge from a well and to provide a check on the integrity of the well (e.g., to identify problems with siltation). Measurements should be made on all wells the first day at the site prior to pumping any well, and again at a well prior to sampling it. On certain sites, water level measurements should be made within a relatively short period of time (i.e., tidally influenced aquifers, aquifers with very flat gradients, etc. [see GSU, 2001]). Instruments used to make the measurements should be capable of obtaining accurate readings to within ± 0.01 foot. An electronic depth-sounding device is preferred for measuring the depth to water. Measurements should be referenced to a marked point, usually the top of the well casing, whose elevation has been surveyed by a licensed surveyor. The depth measuring device must be thoroughly cleaned between wells to prevent cross contamination and maintain sample representativeness (see Section 3.2.4).

3.2.1.3 Detection of Immiscible Layers.

If present in high concentrations, relatively insoluble organic liquids may form either a floating phase (light non-aqueous phase liquid [LNAPL]) on top of well water or a sinking dense layer (dense non-aqueous phase liquid [DNAPL]) depending on the density of the liquid. Samples collected from within the well may contain a mixture of both of these layers and consequently be representative of neither the contaminant layer nor the bulk of the well

water. Determination of the presence of these layers is important in interpretation of ground water data as well as in evaluation of subsurface transport and mitigation measures. Organic liquid-water interface probes can determine the existence and thickness of these layers by lowering the probe into the well before purging or sampling. As a supplement to the interface probe, a transparent bottom-opening bailer can also be used to detect and collect floating layers. If an immiscible layer is detected, its thickness should be recorded and a sample collected.

3.2.1.4 Well Evacuation.

There are essentially two accepted methods for purging groundwater from high and moderate yielding wells: purging large (i.e., three well volumes) or small (i.e., low-flow micropurging) volumes of water from a well prior to sampling.

The concept behind large volume purging is to remove standing water from a well that may not be representative of in-situ ground water quality. Removal of standing water from a well allows fresh ground water from the formation to replace it. The standing water should be drawn down from near the water surface to ensure that fresh water entering the well screen will move upward. While it is generally accepted that well water in the well casing is not representative of the formation water, water in the screened interval of the well may in fact be representative. Low-flow purging/sampling is conducted based on this assumption, but is dependent upon well construction and site hydrogeology. Low flow sampling is a technique that minimizes the hydraulic stress on the aquifer during purging and sampling. This is done by pumping from the screened zone at a low flow rate that will cause minimal drawdown of the water level in the well. Drawdown is measured in the well concurrent with pumping using a water level meter. The use of bailers for purging or sampling is not acceptable for low-flow purging/sampling and is generally discouraged for all types of groundwater sampling.

Large and small volume purging do not require a specific flow rate or purge volume as they are dependent on aquifer conditions. A sample can be collected after the water level and measured field parameters (pH, specific conductance, dissolved oxygen, oxidation-reduction potential, temperature, and turbidity) stabilize over three consecutive readings taken at appropriate intervals. The actual volume of water purged should be based on stabilization of field parameters.

Sampling low yielding wells is problematic. Low yielding wells are defined here as wells that can not sustain a static water level during groundwater extraction at a rate of 100 milliters per minute. It will be possible to completely drain the well using a low pumping rate if the pump draws from the bottom of the well. Exposing the well intake may cause volatilization or chemical reactions to occur resulting in non-representative samples. At no time should the pumping rate be so great as to cause ground water to cascade down the intake screen into the well for either low flow or conventional sampling. Comparative side-by-side sampling is strongly recommended for low yielding wells. For example, in the case of volatile organic compound (VOC) sampling, comparisons could be made between no

purge (i.e., diffusion bags, no purge micropurge), low flow techniques, and large well volume purging. Samples to be analyzed for volatile components should be collected as soon as sufficient water has reentered the well.

Whenever possible, purge rates should not exceed aquifer recharge rates determined from appropriate well testing. Wells should be purged at rates below those used to develop the well to prevent agitation of sediment, to prevent damage to the well, and to avoid disturbing accumulated corrosion or reaction products in the well. A low flow rate will reduce the possibility of volatilizing organic compounds from the water and reduce the likelihood of mobilizing solids in the subsurface that are immobile under natural flow conditions.

Large volume purging collects groundwater from a larger radius around a well screen than does low volume purging. For this reason one should consider if low flow sampling should be compared to large volume purging. If contaminants are only detected by the large volume method, this may suggest the well is not appropriately located for low flow sampling.

Purging of wells is routinely done with submersible positive displacement pumps (i.e., bladder pumps, centrifugal pumps). Use of dedicated equipment is preferred to minimize risk of contaminant introduction into the well and samples, minimize well disturbance and sampling artifacts, reduce the need for sample filtration, minimize the time spent sampling, and reduce the number of equipment blanks. Refer to CALEPA (1995) and Nielsen (1991) for a detailed discussion of different kinds of groundwater sampling devices.

Provision must be made to dispose of the purged water properly.

3.2.1.5 In-Situ or Field Analyses.

Several ground water parameters are physically or chemically unstable and should be tested either in the well, in the sampling/purging line using in-line probes, or immediately after collection using field meters. Examples of unstable field parameters include pH, dissolved oxygen, oxidation-reduction potential, temperature, and turbidity. The preferred method of making these measurements is to insert probes directly into the purge line so that a continuous reading can be taken as water is purged from the well. The final reading is taken when stable values are attained. If in-line probes are not available, then another alternative method is a "down-hole" or in-situ probe which measures field parameters in the well water. Otherwise, groundwater should be brought to the surface during purging, collected in a sample container or cup, and measured quickly with as little contact with the atmosphere as possible.

Field notes and logs taken at this time should include the appearance of the purge water including its color, turbidity (measured in nephelometric turbidity units - NTUs), and odor. Samples which are turbid may not be suitable for analysis and may be indicative of well damage, improper well design, or need for well development.

3.2.1.6 Sample Withdrawal.

Sampling equipment must be constructed of inert material and be used to minimize sample disturbance resulting in changes in water chemistry. Wells should be sampled from least to most contaminated.

There are four broad categories of groundwater sampling devices: grab samplers (e.g., bailers and syringe devices), positive displacement pumps (e.g., bladder and centrifugal pumps), suction lift pumps (e.g., direct line and peristaltic pumps), and gas contact pumps (e.g., gas-lift and gas-drive devices). The CALEPA (1995) document summarizes the capabilities of these different groundwater sampling devises. Table 1 of the 1995 CALEPA document indicates that grab, suction lift, and gas contact devices can be unsuitable for obtaining representative groundwater samples, especially for volatile constituents. To encourage innovation, CALEPA may allow the use of other sampling methods provided it is demonstrated that the method can yield representative groundwater samples on a site-specific basis.

Care should be taken at all times not to agitate ground water in the well or samples allowing volatile or gaseous material to escape. Sampling equipment (especially bailers) should never be dropped into the well or allowed to leak water back into the well as this can cause degassing of the water upon impact.

Ideally, enough purging, sampling, and filtering equipment can be taken to the field so that each item is used in only one well and taken to the lab for thorough decontamination (see Section 3.2.4). If a piece of equipment must be used in more than one well, it must undergo field decontamination procedures and equipment blanks should be collected (see Section 5.0). Clean, powderless gloves should be worn by sampling personnel and should be changed often. A clean plastic sheet should be placed around the well to prevent surface soils from coming in contact with purging equipment and lines, which in turn could introduce contaminants to the well. A plastic bag may be pulled down over the top of the well casing and samples collected through a hole in the bag for further protection during sampling.

Samples should be collected and containerized in the order of volatilization. A collection order recommended by CALEPA (1995) is:

- VOCs
- Semivolatile organic compounds
- Major water quality cations and anions
- Stable isotopes (e.g., oxygen, hydrogen, nitrogen, lead)
- Metals
- Cyanide
- Turbidity
- Radionuclides

3.2.1.7 Filtration.

If turbidity is less than 5 NTU, filtering is not necessary. Samples should never be filtered when a water supply well is sampled. For risk assessment purposes and to assess facility impacts to groundwater, unfiltered samples should also be considered if significant colloidal transport is suspected (Filtered samples may also be collected at the same time for comparison). Filtered samples for dissolved metals analysis should be used whenever groundwater is excessively turbid or, in some cases, to reduce statistical outliers. Poorly designed or developed wells yielding inappropriately high turbidity values should be replaced if re-development does not improve turbidity conditions. Filtration should also not be used to compensate for poor sampling practices.

When filtering is conducted, use of in-line filters is strongly recommended since filtering after groundwater contacts the atmosphere can underestimate metal concentrations due to possible precipitation of metal oxides. The use of 1 micron filters is recommended to allow passage of colloids and filtration of particles greater than clay size. Filters must be discarded after use at each well.

In those instances where in-line filtration is not possible, it may be advisable to collect both filtered and unfiltered samples. Filtering should be done as quickly as possible using positive pressure filtering equipment (laboratory filtration or filtration by vacuum methods are not acceptable).

It is essential that when a sample is filtered for metals, no preservatives/acids be added until after filtration as this will tend to dissolve particulates. Filters should be pre-washed per manufacture's instructions.

3.2.1.8 Field Logs.

One member of the sampling team should be assigned to make observations and record information in field logs and notebook.
Observations recorded should include:

- Collectors' names
- Well identification
- Static water level depth and measurement technique
- Presence of immiscible layers, detection method, and thickness
- Well yield, high or low
- Evacuation procedure/equipment
- Purge volume, pumping rate, and time purged
- Appearance of ground water (color, turbidity, odor, etc.)
- Sample collection procedures/equipment
- Date and time of collection
- Sample treatment and containers
- Parameters requested for analysis
- Field analysis procedures and results

- Sample packing, distribution, and transporter
- Other field observations including climatic conditions and problems encountered
- Photographs
- Date and title of approved sampling plan

3.2.2 Seeps and Springs.

Seeps and springs are generally areas where the ground surface intersects the water table. Because of reactions of the water with microbiological populations and the atmosphere, oxygen content, pH, nutrient and metal concentrations may be quite different from those in the ground water. However, seep and spring analyses can be used in risk assessments and as evidence of contaminant migration if properly interpreted. A scoop, or dipper/pond sampler can be used to collect samples from seeps. The sampler can be gently suspended in the water or laid against the bank and the water will flow with very little additional disturbance into the sampler for transfer to sample bottles. It is important to collect the sample as close to the actual seep as possible to reduce contact time with the atmosphere and potential for surface contamination. In some cases, soil may need to be removed, with appropriate decontaminated tools, up to a foot or two to get enough flow to collect in the sampler. At sites where seeps are repeatedly sampled, it may be advantageous to install shallow wells (<5 feet) which are then purged and sampled as regular monitoring wells.

3.2.3 Surface Waters.

Whereas in ground water sampling the sampling points are determined upon well construction, both location and depth of samples from surface waters must be decided upon before sampling. Usually, standing water (e.g., ponds) cannot be assumed to be well-mixed or uniform in composition. Therefore, the type of sampler used and the care with which it is placed becomes more important. References which discuss the choice of sampler include Ford et al., 1984 (from which much in the following paragraphs is drawn), the U.S. Department of the Interior, 1977, and deVera et al., 1980.

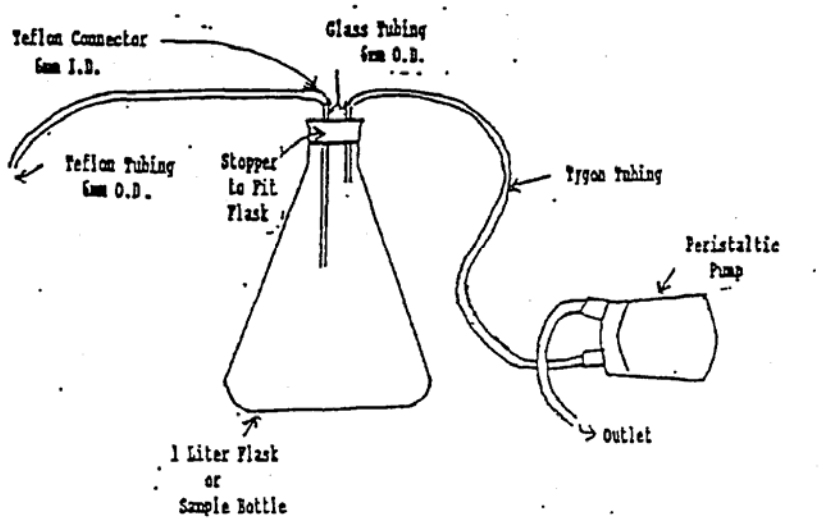
Samples from shallow depths can be readily collected by submerging the sample container. The method is advantageous when the sample might be altered during transfer from a collection vessel into another container. This is the case with samples collected for oil and grease analysis because considerable material in the surface film may adhere to the sample transfer container and as a result produce inaccurately low analytical results. Similarly the transfer of a liquid into a small sample container for volatile organic analysis, if not done carefully, could result in significant aeration and resultant loss of volatile species. If the water is considered to be hazardous, the external surface of each container may need to be decontaminated. Another disadvantage with this method is that the water surface is disturbed at least once for each sample, whereas the use of a larger, transfer sampler will disturb it fewer times.

It is often necessary to collect liquid samples at some distance from shore or the edge of the containment. In this case, a useful device is the pond sampler (deVera et al., 1980) which incorporates a telescoping heavy-duty aluminum pole with an adjustable beaker clamp attached to the end. A beaker or other disposable glass or plastic container, or the

actual sample container itself, can be fitted into the clamp. In situations where cross contamination is of concern, use of a disposable container or the actual sample container is always advantageous. The cost of proper cleaning usually outweighs the cost of disposal of otherwise reusable glassware or bottles. This is especially true when the cleanup must be done in the field. The potential contamination of samples for volatile organic analysis by the mere presence of organic solvents necessary for proper field cleaning (see Section 3.2.4) is usually too great to risk.

Another method of extending one's reach in collecting samples for analyses of nonvolatile organics is the use of a small peristaltic pump. In this method the sample is drawn in through heavy-wall Teflon tubing and pumped directly into the sample container. This system allows the operator to reach out into the liquid body, sample from depth, or sweep the width of narrow streams. Because the interior of the peristaltic pump requires flexible tubing and most flexible tubing is not inert to many hazardous wastes, a vacuum flask can be inserted in line before the pump assembly as shown in Figure 3.2-1. A peristaltic pump can be used to collect samples at depths up to several meters in ponds or other containment vessels. Peristaltic pumps are not recommended for the collection of samples for volatile analysis.

Figure 3.2-1 Peristaltic Pump Sampler (from National Council of the Paper Industry for Air and Stream Improvement, Inc., 1982)



In situations in which samples are required from depths greater than the capabilities of a peristaltic pump (approximately 25 feet), samplers such as Kemmerer, ASTM Bomb (Bacon Bomb), or Van Dorn samplers can be used; however, care must be used in selecting devices that are made of materials that will not contaminate the sample. See Ford et al. (1984) for more details on these samplers. Coliwasa samplers can also be used for surface water samples, especially where uniform samples with depth are required. These are described in Section 3.3, Industrial Waste Sampling. Determination of the locations and depths from which samples should be collected and the appropriate number of samples is discussed in Section 3.1.2.

3.2.4 Decontamination of Equipment.

Laboratory decontamination of sampling equipment is preferable to field decontamination but is not always possible. In general, when a piece of equipment must be cleaned in the field and reused, it should only be used to collect samples expected to be more highly contaminated. It must never be used if it appears discolored or otherwise obviously contaminated.

Nondisposable pumps should be cleaned in the field by pumping a solution of non-phosphate detergent through the pump and associated tubing. This solution should be followed by tap water, then followed by purified water.

Nondisposable bailers should be disassembled and cleaned by washing in non-phosphate detergent, followed by rinses with tap water and deionized water. They should then be air

dried in a clean environment, reassembled using gloves, and wrapped or sealed in a clean plastic bag. When organic compounds are of concern, isopropyl alcohol (rubbing alcohol) should be considered for decontamination, since it has the advantage of drying wet surfaces quickly, dissolving many organic compounds, and being less toxic and less flammable than other solvents.

Filtering apparatus should be of a disposable variety eliminating the decontamination process. In those rare instances filtering equipment is reused, it should be cleaned in a solution of a non-phosphate detergent, followed by rinses with tap water, a dilute nitric acid solution, and finally, deionized water.

Equipment blanks should be collected from all equipment cleaned in the field and reused, to detect any contamination not removed by or introduced by the cleaning procedure.

When equipment is returned to the laboratory or office, it should be thoroughly cleaned. All waste decontamination fluids and materials should be collected and properly disposed.

3.2.5 Quality Control for Water Sampling.

Quality control samples should be collected according to procedures described in Section 5. These procedures are described below more fully as they apply to water samples.

Collocated samples should represent 5% of the samples collected. Usually this means that a second set of samples is taken from one well. This well should be named in the sampling plan, i.e., chosen before sampling begins.

Split samples are more difficult to obtain, because they involve collecting enough sample in an intermediate container to decant into all sample bottles for that analysis. For analysis of volatile components, the sample should be handled as little as possible to minimize loss. VOA bottles should be filled with water from the same bailer, if possible. If the bailer does not hold enough water to fill all VOA bottles needed, then water from each bailer filled should be distributed among all VOA bottles. Field notes should contain information on how the sample was split.

Both collocated and split samples are useful replicate samples to collect. Split samples are used to determine the precision or reproducibility of the analyses. They are especially useful for interlaboratory comparisons. But because of the possibility of loss of constituents during the splitting process, collocated samples may be more accurately reflect in-situ concentrations. These samples may also yield a measure of error from the sampling procedures.

Travel blanks, consisting of distilled water from the laboratory, are used mainly for volatile analyses. They should be brought out to the field in sample containers and returned to the laboratory, one with each cooler, to account for any contamination which may occur from container handling.

Equipment blanks should be taken each day, using distilled water and passing it through each equipment procedure used. Bailers or pump assemblies should have distilled water collected as blanks, filtration units should be sampled, and all preservatives used in the field should be included.

Additional quality control samples are described in Section 5.0.

3.2.6 References.

1) The California Environmental Protection Agency, July 1995. Representative Sampling of Ground Water for Hazardous Substances, Guidance Manual for Ground Water Investigations.
2) Nielsen, David M., 1991. Practical Handbook of Ground-Water Monitoring. Lewis Publishers, Inc.

3) Puls, Robert W., and Barcelona, Michael J., April 1996. Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures. United States Environmental Protection Agency, EPA/540/S-95/504.

4) Geological Services Unit, Geology and Corrective Action Branch, Department of Toxic Substances Control, July 2001. Guidance Document, Monitoring Requirements for Permitted Hazardous Waste Facilities, Appendix B.

3.3 INDUSTRIAL WASTE SAMPLING.

This section covers sampling and analysis for industrial wastes. The discussion of health and safety plans for such activities, although of critical importance, is not included here. The intent is to address the sampling of process wastes, as may occur during facility inspections or site investigations. Future revisions of SW-846 Chapter 10 will provide additional guidance on sampling techniques.

3.3.1 General Considerations.

In contrast with groundwater sampling, which was discussed in the previous section, industrial waste sampling generally involves concentrated liquids, solids, slurries, or sludges. The choice of sampling technique depends on the physical state and the chemical composition of the waste. The Field Manual of SW-846 and the EPA Manual "Samplers and Sampling Procedures for Hazardous Waste Streams" provide some guidance in sampling techniques. In addition, the American Society for Testing and Materials (ASTM) has published numerous Standard Methods for sampling commercial products and wastes. For waste piles, reference ASTM D 6009-96 titled "Standard Guide for Sampling Waste Piles". This standard may be obtained from ASTM through their web site: http://www.astm.org

3.3.2 Material Compatibility.

Because of the concentrated nature of the waste, chemical compatibility is an important issue in the choice of sampler. In general, glass or Teflon are acceptable materials for sampling of concentrated wastes. Table 3.3-1 from SW-846 lists some acceptable samplers for given sampling situations.

3.3.3 Choice of Sampling Technique.

As is obvious from Table 3.3-1, the choice of sampling technique will be determined by the waste container. In most cases, the goal is to obtain a sample which is representative of the waste unit. For example, drum sampling should produce samples which include all layers in the drum, since drummed material is often stratified. Sampling techniques may need to be modified for particular sampling situations. The sampling of a large number of drums of unknown material may indicate that sampling with disposable glass thieves is preferable to sampling with a reusable Coliwasa, due to potential chemical incompatibility and difficulties in cleaning samplers between samples. Disposable glass Coliwasa are also available commercially (e.g., from Pollution Abatement Consultants and Services, P.O. Box 1039, Millville, New Jersey 08332) and can eliminate some of the problems of cross-contamination and sampler cleaning.

Sampling of unknown industrial waste should be done simultaneously with some field screening. This serves two purposes: first, it guides sampling by identifying wastes with similar properties, and allows for a refinement of sampling plans. Second, it can identify waste properties and guide subsequent lab analysis requests. Field screening can also identify potential problems which should be addressed in the field, such as the discovery of water-reactive wastes. All pertinent field information on waste characteristics should be transmitted to the lab which will be doing the analysis. Table 3.3-2 lists field measurements and the corresponding lab analysis for a variety of chemicals.

Due to the potential for cross-contamination, dedicated sampling equipment should be used for sampling different waste types when feasible. If samplers are to be used repeatedly, clean the equipment with appropriate solvents. The choice of cleaning solvents depends on the waste and the expected chemical analysis. For the sampling of unknown organics, isopropanol rinses are recommended. When doubt exists as to the cleanliness of sampling equipment, a solvent rinse (equipment blank) can be submitted to the lab along with samples for chemical analysis.

Highly stratified heterogeneous wastes, e.g., globules of oil mixed with soil, should be sampled by collecting samples of each stratum. This is because

1) conventional sampling techniques may not be effective, and

2) an average value for the waste would not be valuable in predicting the properties of individual samples.

The American Society for Testing and Materials (ASTM) has published a standard guide on Sampling strategies for heterogeneous Wastes which can be found in the References at the end of this section.

	Waste Location or Container								
WASTE TYPE	DRUM	SACKS AND BAGS	OPEN-BED TRUCK	CLOSED-BED TRUCK	STORAGE TANKS OR BINS	WASTE PILES	PONDS, LAGOONS, AND PITS	CONVEYER BELT	PIPE
FREE-FLOWING LIQUIDS AND SLURRIES	Coliwasa	N/A	N/A	Coliwasa	Weighted Bottle	N/A	Dipper	N/A	Dipper
SLUDGES	Trier	N/A	Trier	Trier	Trier	a	a		
MOIST POWDERS OR GRANULES	Trier	Trier	Trier	Trier	Trier	Trier	Trier	Shovel	Dipper
DRY POWDERS OR GRANULES	Thief	Thief	Thief	Thief	a	Thief	Thief	Shovel	Dipper
SAND OR PACKED POWDERS OR GRANULES	Auger	Auger	Auger	Auger	Thief	Thief	a	Dipper	Dipper
LARGE-GRAINED SOLIDS	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Trier	Dipper

[a] This type of sampling situation can present significant logistical sampling problems, and sampling equipment must be specifically selected or designed based on site and waste conditions. No general statement about appropriate sampling equipment can be made.

Table 3.3-1

AVAILABLE INFORMATION	ANALYTICAL REQUEST
Suspect high levels of volatile organics (high field readings on explosivity meter, OVA, or PID)	Headspace VOA and Flash Point. (If VOA results show organics of concern, a request should be submitted for specific analyses, e.g., purgeable halocarbons, purgeable aromatics, etc.)
Positive CLOR-N-OIL™	Chlorinated pesticides and PCBs, TOX
High (>1,000 ppm) CLOR-D-TECT™ result	Total halogens
Positive Enzytec ET-10 test	Organophosphates and/or carbamates
Positive PCB immunoassay	PCBs
Positive Beilstein test	Chlorinated pesticides and PCBs
Elevated radioactivity	Gross alpha and Gross Beta radioactivity
Extreme field pH (<3 or >11)	pH
High field sulfide test result	Total sulfides
High field cyanide test result	Total cyanides
Suspect high levels of toxic metals	Metals, WET if necessary

Table 3.3-2. Guide to Requesting Analysis

3.3.4 References

1) ASTM Standard Guide on Sampling Strategies for Heterogeneous Wastes, D5956-96

3) U.S.E.P.A., Characterizing Heterogeneous Wastes, EPA 600/R-92/033, February, 1992

3.3.5 Wipe Sampling.

3.3.5.1 Application.

In some situations, it is necessary to measure the contamination of a surface. Surface contamination measurement may be necessary to:

Verify equipment decontamination, e.g., as part of a clean closure.

Estimate the level of particulate fallout, e.g., from dust fall.

Determine the extent of residual contamination of PCBs after a clean-up.

3.3.5.2 Wipe Procedure

SW-846 does not contain a standard wipe sampling procedure, but the field manual of the Occupational Health and Safety Administration (OSHA), 1990, does specify a procedure to be followed. Some details are shown in that manual. EPA has published a procedure in regulation for wipe sampling following a PCB spill.

The factors to consider in wipe sampling are the wipe material, the solvent, the sampling area, and the use of blanks.

The solvent applied to the wipe material will depend on the contamination being investigated. For PCBs, chlorinated solvents, or semi-volatile organics, a glass fiber filter (37 mm) wetted with hexane or another organic solvent is recommended. Paper filters moistened with acidified deionized water may be used for metals and other analysis.

The area for the wipe sample should be carefully measured and the margin for error estimated. Typically, a 10 cm X 10 cm (100 cm^2) area is wiped. For quality control, replicate wipe samples should be taken from the same general area. The wipes should be placed in containers as described in Section 3.6.

Field blanks should always be used. These would be wipes moistened with the same solvent and placed in the same type of container as the samples. A field blank should be submitted to the laboratory with each batch of wipe samples.

3.3.5.3 Interpretation

The lab results for a wipe sample should be in units of mass, e.g., mg or ug per wipe sample. The actual proportion of contaminant recovered by wiping with a solvent cannot be measured, although studies have shown that 80% of a lead contamination can be recovered from a smooth surface (Chavalitnitikal, 1984).

The surface concentration can then be calculated using the known surface area of the wipe and converting to units of mass per unit area, e.g., mg/m^2. If results in units of

concentration, e.g., mg/kg, are needed, then the lab must provide pre-weighed (tared) wipes.

3.3.5.4 References

1) Chevalitnitikal, Chaiyuth A., "A laboratory evaluation of wipe testing based on Lead Oxide Surface Contamination," Am Ind Hyg Assoc J, 45(5), pp 311-317, 1984.

2) EPA, 40CFR "Subpart G-PCB Spill Cleanup Policy," 761.123 Definitions.

3) OSHA, "Chapter 2; Sampling for Surface Contamination," Volume VI - OSHA Technical Manual, March 26, 1990.

3.4 SOIL SAMPLING.

The following discussion gives a brief description of surface and near surface soil sampling primarily based on the references listed in subsection 3.4.5. The reader should consult those references for more detailed information.

3.4.1 General Considerations.

The selection of sampling techniques and sampling devices for soils should take into account the following points:

1) The objectives of the sampling effort which will determine the number of samples to be collected, the required sampling depth and whether or not the samples are to be composited. See Section 3.1 for additional discussion of sampling plans.

2) The physical properties of the soil, e.g., grain size, cohesiveness, homogeneity and presence of anomalies, such as animal burrows, large rocks or plant roots. Certain samplers which work well with soft, fine-grained soils may not work with hard, rocky soils.

3) Thickness of the soil layer above the bedrock or water table which may limit the depth from which samples can be collected.

4) The amount of sample required. The minimum sample size is specified by the laboratory on the basis of the analytical method and the required sensitivity of analysis.

5) The type(s) of elements or compounds for which the samples will be analyzed. This consideration may preclude the use of samplers made of certain materials (e.g., certain metals, PVC).

Samples should not be collected immediately after heavy rainfall, when the soil is frozen, or in extreme winds (Barth and Mason, 1984b).

3.4.2 Preparation of the Sampling Site.

If the soil layer at a given sampling site is covered with vegetation or other non-soil matter, any such soil cover is removed using a spade, shovel or scoop. The same precautions with respect to structural materials described for samplers in section 3.4.4.1. must be taken with these tools.

An area large enough to collect all samples to be taken at the site (e.g., for subsequent compositing) should be cleared before beginning to sample.

3.4.3 Sample Compositing.

When the major concern of the sampling effort is to establish the distribution of contaminants between different soil horizons or their paths of migration within the soil layer, the collected samples should not be composited.

When the major concern is to obtain a sample which is representative for a particular site, it is recommended that four or more different samples taken at the site be composited into a single sample (Barth and Mason, 1984b). Equal amounts of the different samples should be used for compositing.

NOTE: Compositing effectively raises the detection limits for all potential contaminants at the site because localized high levels of contamination are diluted by mixing with relatively uncontaminated soil.

3.4.4 Sampling Devices.

3.4.4.1 Sampler Materials.

Most commercially available samplers for soil are made of steel, brass or plastic. When gardening tools, such as spades, shovels or trowels are employed, implements made of nickel- or chromium- plated steel should be avoided since the coating may flake off and severely affect the results of trace element analyses.

Painted surfaces are even more subject to abrasion and paint may interfere with determinations of organics and/or trace metals. Plated or painted implements can be used in many cases, however, if the surface coating is removed, e.g., by sandblasting (Ford et al., 1984).

Plastic materials are frequently used as liners of coring samplers; while such liners may be appropriate for soils needing metal analyses, plastic materials are usually not suitable when samples are collected for organic analysis.

Because of the above considerations, it is generally advisable to use samplers which are made of as few materials as possible in order to reduce the number of potential contamination sources. The possibility of contamination from plasticizers should always be considered.

3.4.4.2 Sampler Types.

This section is limited to sampling devices which can be employed with a minimum of special training, equipment or cost. Depending on the physical properties of the soil, sampling depths are limited to 5 meters (Veihmeyer sampler). Sampling to greater depths and under difficult soil conditions usually require drilling equipment and experienced drilling personnel.
An overview hand operated sampling devices for different sampling depths are given in

Table 3.4-1. Detailed descriptions of the use of these samplers can be found in the references indicated in the table.

Ford and coworkers (1984) have given good concise descriptions of a method for near-surface sampling using a spade and scoop and a method for sampling at intermediate depths using an auger and thin-wall tube samplers.

3.4.4.3 Sampler Cleaning and Decontamination.

In order to minimize the contamination of soil samples by the sampling equipment or through cross-contamination, all equipment must be thoroughly cleaned before their first use and also between samples.

The following is a suggested procedure that have been used effectively at the field sites. (Reference 5)

1. Wash and scrub tools with tap water using pressure hose or pressurized stainless steel, fruit tree sprayer. If necessary use a steel brush or other brush to remove adhered soil such as sticky clays. A steam cleaner has been proven to be very effective at this step in the cleaning operation.

2. If organics are present, rinse with the waste solvents from the steps outlined below. Discard contaminated solvent by pouring into a waste container for later disposal.

3. Air dry the equipment or dry with acetone.

4. Double rinse with distilled water.

5. If organic pollutants are of concern, rinse with spectrographic grade acetone saving the solvent for use in step 3 above.

6. Rinse twice in spectrophic grade hexane, saving the solvent for used in step 3 above. Methanol can be used if proper precautions are taken.

7. Air dry the equipment.

8. Package in plastic bags and/or pre-cleaned aluminum foil.

9. Collect contamination blanks to insure that sampling equipments are properly cleaned.

Many disposable samplers are available which minimize the possibility of cross-contamination.

SAMPLING DEPTH	SAMPLER TYPE	APPLICATION	REFERENCES
Near Surface (0-6 inches)	Trowel or Scoop	Top 10 cm only	2,3
	Shovel or Spade	Wide variety of soil condition	3
Mid-Depth (0-72)inches	Trier	Difficult to use with hard, rocky soils	1,2
	Ring lined sampler	Cohesiveness, wet to medium soil	5
	Soil probe or King-tube	cohesive, soft soils; representative samples in soft to medium cohesive soil & silts	6
	Thin-walled tubes	cohesive, soft soils; special tips for wet or dry soils	6
	Soil Recovery Probe	Cohesive soft soils; cores are collected in reusable liners	6
	Peat Sampler	Wet, fibrous, organic soils	6
	Screw Bucket Auger	Cohesive, soft or hard soils	6
	Standard Bucket Auger	General soil	6
	Sand Bucket Auger	Retain dry, loose or granular material (silt, sand & gravel)	6
	Mud Bucket Auger	Wet silt and clay soil	6
	Dutch Auger	Wet, fibrous or rooted soils	6
	In Situ Soil Recovery Auger	Collection of soil samples in reusable liners	6
	Eijkelcamp Stoney Soil Auger	Stoney soils and asphalt	6
	Planer Auger	Used to clean out and flatten the bottom of predrilled holes	6
	Post-Hole/Iwan Auger	Cohesive, soft, or hard soils	6
	Silage Auger	Silage pits and peat bogs	6
	Spiral Auger	Removes rock from auger holes	6
Deep Samples (>72 inches)	Veihmeyer sampler	Cohesive soil to depth of 3 meters (118 inches)	2, 6

Table 3.4-1: Overview of Hand operated soil sampling devices.

3.4.4.4 Soil Sampling for Volatile Organics

Because of the potential to lose volatiles during sampling, storage, and subsampling in the laboratory, special sampling procedures are needed for volatile organics in soil.
The tube type samplers such as Shelby tubes and split spoon samplers can be used for initial sampling for volatile organics. These samplers can collect a relatively undisturbed, intact soil sample; a sub-sample should be taken immediately. For high level (<200 ug/kg) analysis, a sample is taken with a hermetically sealed sampler or preserved with methanol. For low level analysis, the sample is taken in a hermetically sealed sampler or transferred into a VOA vial with sodium bisulfate, water, and a stirring bar, which can be used directly in purge-and-trap analysis, as described in EPA Method 5035.

3.4.5 References.

1) Barth, D.S. and B.J. Mason. 1984a. Soil Sampling Quality Assurance Guide. EPA-600/4-84-043

2) Barth, D.S. and B.J. Mason. 1984b. Soil Sampling Quality Assurance and the Importance of an Exploratory Study. In: Environmental Sampling for Hazardous Wastes, G.E. Schweitzer and J.A. Santolucito, eds., ACS Symposium Series 267, ACS, Washington, D.C.

3) Mason, B.J. 1983. Preparation of Soil Sampling Protocol: Techniques and Strategies. EPA-600/4-83-020. Environmental Monitoring Systems Laboratory, U.S. EPA, Las Vegas, NV.

4) EPA, "Behavior and Determination of Volatile Organic Compounds in Soil: A Literature Review," EPA 600/R-93/140, EMSL-Las Vegas, May, 1993.

5) Mason, B. J. Preparation of Soil Sampling Protocols: Sampling Technique and Strategies. EPA/600R-92/128, EMSL-Las Vegas, July 1992

6) EPA, "Description and Sampling of Contaminated Soils", EPA/625/12-91/002, November 1991.

3.5 SOIL GAS.

Soil gas measurements can be extremely important in evaluating site contamination. Volatile organics will partition among soil, water, and soil gas depending on their volatility, water solubility, and affinity for soil.

Information on soil gas is useful in defining soil contamination related to: land-filled hazardous materials; contaminated ground water including leachate plumes from landfills; and leaking underground fuel tanks.

Soil gas sampling is particularly difficult to do accurately because in making the measurement we disturb the soil and soil structure. Since we expose fresh soil surfaces to the atmosphere, steep gas concentration gradients develop and the soil rapidly "off-gases".

The discussion provided here outlines methods which have been used, without making specific recommendations. More detailed protocols have been published by the Los Angeles Regional Water Quality Control Board (Ref 1) and the U.S. EPA Emergency Response Team (Ref 2).

Several new passive and active soil gas sampling techniques have been developed in conjunction with push technologies for sub-surface investigations.

3.5.1 Bore Hole Gas Probe Sampling Technique.

Soil gas can be sampled at various depths in the soil profile using bore hole techniques. One procedure which has proven useful is the bore hole probe technique in which a 2-4 inch diameter hole is made by augering to the depth of interest. A hollow probe with a perforated tip is then driven about one foot into the soil at the bottom of the hole allowing soil gas at that depth to be pumped to the surface with a peristaltic pump. The gas sample is then collected in a gas collection bottle located between the probe and the pump. A flow meter is needed since it is important that the pumping rate does not exceed 10-100 mL/minute. Excessive flow rates create a partial vacuum and draw clean air into the soil, diluting the sample. A problem occasionally encountered is ground water, which if reached will be sucked into the gas collection bottle and contaminate the sampling device.

A small hollow stem auger (6" in diameter with a 3" inside diameter) can be useful for depth specific sampling at depths too great for a hand auger. Drilling is stopped at specified depths and sampled by the bore hole technique. (This procedure requires a cooperative drill rig operator.)

3.5.2 Sealed Bore Hole Technique.

The sealed bore hole technique does not allow soil gas to be sampled at various depths in the soil profile, but rather gives a depth-averaged soil gas sample. This technique usually gives sufficient information for a preliminary characterization of soil gas at the site. There are several variations to the sealed bore hole technique. One is to auger a 6-12" deep hole and insert a 3/4" in diameter Teflon^{R} probe with holes drilled at the tip to avoid plugging. The probe is attached by various fittings to a peristaltic pump as in Section 3.5.1.

For sampling at greater depths, insert the sampling probe into a 3-5 foot deep bore hole (about 2" in diameter) and pack topsoil around the probe. An aluminum foil plate with a hole for the sampling tube is placed at the top of the sample hole and covered with soil to seal the chamber. The sampling probe should be extended about half way down the bore hole. Allow 24-48 hours for the soil gas in the auger cavity to reach equilibrium with the surrounding soil and sample as in Section 3.5.1.

A simple technique for sampling uses a small (3/8") diameter steel rod to create an open hole at the desired depth. The rod is removed and a 1/4" diameter stainless steel probe is inserted into the open hole. Topsoil is packed around the tube to seal the system from ambient air. The gas can then be sampled as in Section 3.5.1. or drawn into a Tedlar bag located in a vacuum desiccator The small rod is easier to drive and allows sampling in otherwise inaccessible areas.

3.5.3 Headspace Technique.

This technique is the most difficult because of major losses of the most volatile constituents. As a result, this technique may be most valuable for qualitative rather than quantitative measurements. The sample can be fully characterized by GC/MS in the laboratory, but the concentrations reported are likely to underestimate the most volatile contaminants.

In the headspace technique, sufficient subsurface soil is collected in a glass jar with a Teflon lined septum to fill the jar to at least ½ the total volume. The jar is then transported to the laboratory and the headspace is sampled directly by syringe.

3.5.4 Solid Sorbent Sampling Technique.

This technique adsorbs the soil gases on a solid matrix (i.e., tubes containing Tenax-GC, activated charcoal, or XAD-2) in the field and then desorbs the sample in the laboratory. The soil gas can either be pumped across the sorbents or allowed to diffuse passively over a period of time. Low flow monitoring pumps must be capable of maintaining consistent flows at prescribed rates. Characteristics of the compound(s) and sorbent of interest should be investigated thoroughly before attempting this procedure. For example, the optimum volume of gas and rate of pumping will depend on target compounds, sorbent, detection limits, and expected concentrations.

3.5.5 Construction of Samplers.

Samplers should be constructed of stainless steel or Teflon. Tygon, rubber, and other types of tubing are to be avoided because they may give inaccurate results due to adsorption and release of volatiles. Gases adsorb and desorb from Teflon to a certain extent, and for this reason stainless steel is preferable.

3.5.6 Cleaning of Sampling Equipment.

The sampling device should be cleaned with a detergent, rinsed with deionized water, and dried in a clean environment before performing any field work. If necessary, rinse the sampling device with deionized water between samples, followed by purging (blowing out) with hydrocarbon free air. Pumping ambient air through the system must be verified as an effective means of cleaning.

3.5.7 Quality Control.

Quality control samples should include field blanks (ambient air or hydrocarbon free air) to check for sample carryover, duplicates taken from the same bore hole, a standard reference gas if available, and spiked samples when appropriate.

3.5.8 Portable Vapor Detectors.

There are various commercially available portable direct reading vapor detectors (PVD) which are useful for rapid field evaluation. The photoionization detector (PID) is a vapor detector which has adequate sensitivity for organics like benzene (0.5 ppm) and halogenated solvents, but does not detect methane. Its use is very straightforward-- to evaluate soil gas a 12" hole is augered and the PID probe is inserted and read. Only highly contaminated sites can use this method. Another useful PVD is the Century OVA 128 (with a flame ionization detector, FID) which, unlike the PID, responds to all volatile organics about equally. The OVA can be operated in continuous, total, or GC modes and thus has the ability to differentiate some components of the gas mixture.

The PVDs are most useful for rapid, preliminary site assessments. Typical applications include:

1) Location of "hot" spots.
2) Crude definition of depth profile (for example, surface spills can be distinguished from land-filled barrels).
3) Screening wells for contamination.
4) Field guidance to crews drilling wells.
5) Protecting the health and safety of field staff.

3.5.9 Soil Gas References

1. California Regional Water Quality Control Board, Los Angeles Region, "Requirements for Active Soil Gas Investigation, Well Investigation Program," March, 1994.

2. U.S. EPA Office of Solid Waste and Emergency Response, "Compendium of ERT Soil Sampling and Surface Geophysics Procedures," EPA/540/P-91 006, January, 1991.

3.6 CONTAINERS.

Specific containers are required for some tests. Generally, samples for organic analysis are collected in glass containers. Glass containers are free of organic plasticizers. Certain organics which are sensitive to light and decompose easily are collected in amber glass containers. Samples for inorganic (metals and anions) analysis are generally collected in plastic or glass containers.

3.6.1 Sample Containers.

The Sampling and Analysis Plans should identify the type of containers to be used for sample collection. When none are specified, the following guidelines will apply:

Type:

When organics are the analytes of interest, glass bottles with Teflon-lined caps should be used. When metals are the analytes of interest, polyethylene containers with polypropylene or polyethylene caps should be used. Glass bottles with Teflon-lined caps may also be used for metals.

Several common container types are listed on the reverse side of the Sample Analysis Request form (fig. 4.0-4).

Size:

1) For soils and wastes, 8 oz. wide-mouth jars with Teflon closures should generally be used. Filling the container half full will provide sufficient sample for most analyses. However, for soils and wastes requiring volatile organic analysis, a 4 oz. wide-mouth jar (filled to capacity to minimize headspace) will suffice. See also Table 3.7-2 in Section 3.7.

2) Containers for water samples are specified in Table 3.7-3 in Section 3.7.

3.6.2. Container Cleaning.

Containers may be purchased pre-cleaned and certified and are preferred to in-house cleaning. These containers may be purchased from the following sources:

I-Chem Research Inc.
2 Bouilen Circle, Suite 8
New Castle, DE 19720
1-(800) 262-5006

Scientific Specialties Service
P.O. Box 352
Randalstown, MD 21133
1-(800) 648-7800

Eagle Picher
36 BJ Tunnel Blvd.
Miami, OH 74354
1-(800) 331-7425

Environmental Sampling Supply
9601 San Leandro Blvd.
Oakland, CA 94603
1-(800) 233-8425
1-(510) 562-4988

When pre-cleaned and certified containers are not available, the containers should be cleaned to suit the type of analysis required. When samples are to be analyzed for metals (e.g. Method 6010, SW-846), the cleaning procedure for containers and closures should be:

1) Thoroughly wash with non-phosphate detergent (e.g. Liquinox) and hot tap water.
2) Rinse three times with tap water.
3) Rinse with nitric acid (1:1).
4) Rinse three times with ASTM Type II water.
5) Glass, oven dry; plastic, air dry.

When samples are to be analyzed for organics glass containers are required. The cleaning procedure for the containers and closures should be:

1) Thoroughly wash with non-phosphate detergent and hot tap water.
2) Rinse three times with tap water.
3) Rinse with nitric acid (1:1).
4) Rinse three times with ASTM Type II water.
5) Rinse with methylene chloride.
6) Oven dry.
7) Bake at 400°C. (when required).

Other cleaning procedures may be used when required by the Sampling and Analysis Plan. For example, it may be necessary to delete the use of methylene chloride when analyzing for volatile organics.

A modified procedure may be used if it can be documented through an active analytical quality control program using spiked samples and field blanks that the procedure is adequate for its intended use.

3.7 SAMPLE PRESERVATION.

3.7.1 Preservation.

The Sampling and Analysis plan should identify sample preservation methods that are to be used. Where none are specified, the requirements given below should be used.

Methods of sample preservation are relatively limited and are generally intended to 1) retard biological action, 2) retard hydrolysis, and 3) reduce absorption effects. Preservation methods are generally limited to pH control, chemical addition, refrigeration (4°C.), and freezing (-15°C.).

3.7.2 Preservation of Soil and Waste Samples.

Preservation of soil and wastes is generally limited to refrigeration. High level samples for semivolatile and metal analysis (those with analyte concentrations above 1%) generally do not require preservation. Low level (<10 mg/kg) to mid level (10 to 10,000 mg/kg) samples generally require preservation by cooling to 4°C. See Table 3.7-2.

3.7.3 Preservation of Water Samples

Preservation for water samples is given in Table 3.7-3.

Table 3.7-2 Sampling and Preservation for Soil and Wastes

PARAMETER	CONTAINER[a]	PRESERVATION	HOLDING TIME	SAMPLE SIZE
Acidity	P,G	Cool, 4°C		4 oz jar
Alkalinity	P,G	Cool, 4°C		4 oz jar
Chloride	P,G	None		4 oz jar
Chromium VI	P,G	Cool, 4°C	30 days (EPA 3060A)	4 oz jar (fill to minimize headspace)
Conductivity	P,G	Cool, 4°C		4 oz jar
Cyanide (Total & amenable to chlorination)	P,G	Cool, 4°C	14 days	4 oz jar (fill to minimize headspace)
Cyanide (Reactive)	P,G	Cool, 4°C store in dark	Analyze as soon as possible	4 oz jar (fill to minimize headspace)
Fluoride	P,G	None		4 oz jar
Nitrate	P,G	Cool, 4°C		4 oz jar
Organolead	G-Amber	Cool, 4°C	14 days	4 oz amber glass (fill to minimize headspace)
pH	P,G	None	Analyze as soon as possible	4 oz jar
Sulfate	P,G	Cool, 4°C		4 oz jar
Sulfide (Total)	P,G	Cool, 4°C Fill surface of solid with 2N Zn acetate until moistened	Analyze as soon as possible	4 oz jar (fill to minimize headspace)
Sulfide (Reactive)	P,G	Cool, 4°C store in dark	Analyze as soon as possible	4 oz jar (fill to minimize headspace)
Extraction Procedure Toxicity	Glass, Teflon-lined Septum	Do not add preservative. Refrigerate only if sample integrity is not affected		1 L for liquid sample, 200 g for solid sample
TCLP	Glass, Teflon-lined Septum	same as above	Vol & semi-vol-14 days Hg-28 days Metals (except Hg)-180 days, see footnote d	Liquid sample: 1 L minimum for each category of analysis; Solid sample: 250 g
Total Phosphate	P,G	Cool, 4°C		4 oz jar

Table 3.7-2 Sampling and Preservation Requirements for Soil and Wastes (continued)

PARAMETER	CONTAINER[a]	PRESERVATION	HOLDING TIME	SAMPLE SIZE
Total Metals (except Cr VI and Hg)	P,G	None	6 months (except Hg, 28 days)	4 oz jar
Volatile Organics: soil, sediments & sludges	Single transfer sampler (eg. Encore ™) **For field preservation call ECL**	Cool, 4°C.	48 hours Note: High level preserved in MeOH within 48 hours extends to 14 days	low level-5 g size<200 ug/Kg high level-25 g size >200 ug/Kg
Volatile Organics: concentrated wastes	G	Cool, 4°C.	14 days	4 oz jar (fill to minimize headspace)
Semivolatile Organics: soil, sediments & sludges	G	Cool, 4°C	14 days to extract; 40 days to anal. after extraction.	8 oz widemouth jar (1/2 full)
Semivolatile Organics: concentrated wastes	G	None	14 days to extract; 40 days to anal. after extraction.	8 oz widemouth jar (1/2 full)
PCDD/PCDF	G	Cool, 4°C	1 year to extract; 40 days to anal. after extraction	8 oz widemouth jar (1/2 full)

[a] P =Polyethylene container with polypropylene closure.
G = Glass container with Teflon-lined closure.
G-V = Glass VOA vial or bottle with Teflon septum

[b] Minimum volume for analysis shown in ( ).
For VOA samples intended to be submitted to the laboratory in end-capped core tubes, there is evidence that preserving by freezing with dry-ice is superior to preserving by cooling to 4°C. Contact ECL for details.
Ref.: Data from P. King, P & D Environmental.

[c] There is evidence that VOA soil samples preserved in methanol during the field sampling and cooled to 4°C is superior to simply preserving by cooling to 4°C. However, the methanol used for preservation must be absolutely pure in order to avoid introducing volatile contaminants. A field blank is also required. Contact the laboratory for preservation details and sample handling procedure.
Ref.: *Environ. Sci. Technol.*, **1990**, 24, 1387-1392.

[d] Maximum sample holding times from field collection to TCLP extraction. See Method 1311 for the preparative and analysis holding times for TCLP extracts.

Table 3.7-3 Sampling and Preservation for Water and Wastewater

PARAMETER	CONTAINER[a]	PRESERVATION	HOLDING TIME	SAMPLE VOL, mL(minimum)[b]
Acidity	P,G	Cool, 4°C	14 days	100 (100)
Alkalinity	P,G	Cool, 4°C	14 days	100 (100)
Ammonia	P,G	Cool, 4°C H_2SO_4 to pH <2	28 days	1000 (500)
Asbestos	P	Cool, 4°C	48 hours	1000 (1000)
Boron	P,G	none	28 days	100
Chloride	P,G	none	28 days	100 (50)
Chromium VI	P,G	Cool, 4°C	24 hours	500 (200)
Conductivity	P,G	Cool, 4°C	24 hours	100 (50)
Cyanide (Total & amenable to chlorination)	P,G	Cool, 4° C, 10 N NaOH to pH>12; 0.6g Ascorbic acid/L if Cl present or 5 ml 0.1 N sodium arsenite/L	14 days	1000 (500)
Cyanide (Reactive)	P,G	May adjust to pH 12 with NaOH but sample integrity maybe affected. Cool, store in the dark.	Analyze as soon as possible	100 (100), fully filled with zero headspace.
Hardness, Total	P,G	HNO_3 to pH <2	6 months	100 (50)
Fluoride	P,G	none	28 days	300 (100)
METALS (except Cr VI and Hg):				
Dissolved	P,G	Filter onsite HNO_3 to pH <2	6 months (except Hg, 28 days in glass, 13 days in plastic)	1000 (500)
Total	P,G	HNO_3 to pH <2	6 months (except Hg, 28 days in glass, 13 days in plastic)	1000 (500)
Nitrate	P,G	Cool, 4°C	48 hours	50 (50)
Nitrite	P,G	Cool, 4°C	48 hours	50 (50)

Table 3.7-3 Sampling and Preservation for Water and Wastewater (Continued).

PARAMETER	CONTAINER[a]	PRESERVATION	HOLDING TIME	SAMPLE VOL, mL(minimum)[b]
pH	P,G	None	Measure in Field; 24 hours	50 (25)
Organolead	G-Amber with Teflon-lined	Cool, 4°C	14 days	1000, fully filled with zero headspace
Ortho-Phospate	P,G	Cool, 4°C	48 hours	50 (50)
Phosphate, Total	P,G	Cool, 4°C H_2SO_4 to pH <2	28 days	50 (50)
Silica	P,G	Cool, 4°C	28 days	50 (50)
Solids, Total Dissolved	P,G	Cool, 4°C	7 days	100 (50)
Sulfate	P, G	Cool, 4°C	28 days	50 (50)
Sulfide (Total)	P, G	Cool,4° C, 4 drops or more/100 ml of 2 N Zn acetate, 6 N NaOH to pH >9	7days	1000 (500) fully filled with zero headspace
Sulfide (Reactive)	P,G	May adjust to pH 12 w/ NaOH and add Zinc acetate but integrity of sample maybe affected, cool, store in dark.	Analyze as soon as possible.	100 (100), fully filled w/ zero headspace.
ORGANICS				
Semivolatile Organics (8270) (no residual chlorine present) Semivolatile	G	Cool, 4°C	7 days to extract; 40 days to anal. after extraction.	1-gal. or 2-1/2 gal. amber glass with Teflon liner
Semivolatile Organics (8270) (residual chlorine present)	G-Amber	Add 3ml of 10% sodium thiosulfate per gallon; Cool, 4°C	7 days to extract; 40 days to anal. after extraction.	1-gal. or 2-1/2 gal. amber glass with Teflon liner
Purgeable Organics (8260) (no residual chlorine present)	G(40 ml VOA vial with Teflon-lined septum cap	Adjust to pH<2 (see footnote c); Cool, 4°C	28 days	2- 40 ml VOA vials fully filled with zero headspace

Table 3.7-3 Sampling and Preservation for Water and Wastewater (Continued).

PARAMETER	CONTAINER[a]	PRESERVATION	HOLDING TIME	SAMPLE VOL, mL(minimum)[b]
Purgeable Organics (8260) (residual chlorine present)	G(40 ml VOA vial with Teflon-lined septum cap)	Cool, 4°C, adjust to pH<2, see footnotes c & d	14 days	2- 40 ml VOA vials fully filled with zero headspace
Purgeable Aromatics	G-V	Cool, 4°C, Adjust to pH<2, see footnotes c & d.	14 days	2 x 40 (40) vials fully filled with zero headspace
Purgeable Halocarbons	G-V	Cool, 4°C, see footnote d	28 days	2 x 40 (40) vials fully filled with zero headspace
Acrolein & Acrylonitrile	G-V	Cool, 4°C, pH 4-5, see footnote d	14 days	2 x 40 (40) vials fully filled with zero headspace
Gasoline/Diesel/TPH	G-V	Cool, 4°C HCl to pH<2, see footnotes c & d	28 days	2 x 40 (40) vials fully filled with zero headspace
N-Methyl-carbamate pesticides	G	Cool, 4^0 C, pH 4-5 with 0.1N chloro-acetic acid	7 days to extract; 40 days to anal. after extract.	1000 (1000)
Pesticides	G	Cool, 4°C,	7 days to extract; 40 days to anal. after extraction.	1000 (1000)
PCB	G	Cool, 4°C	7 days to extract; 40 days to anal. after extraction.	1000 (1000)
PCDD/PCDF	G	Cool, 4°C, see footnote d	7 days to extract; 40 days to anal. after extraction.	1000 (1000)
PAH (polynuclear aromatic hydrocarbons)	G	Cool, 4°C, store in dark, see footnote d	7 days to extract; 40 days to anal. after extraction.	1000 (1000)
Formaldehyde	G	Cool, 4°C,	7 days to extract; 40 days to anal. after extract.	500 (1000)
Chlorinated Phenols	G	Cool, 4°C, see footnote d	7 days to extract; 40 days to anal. after extraction.	1000 (1000)

Table 3.7-3 Sampling and Preservation for Water and Wastewater (Continued).

PARAMETER	CONTAINER[a]	PRESERVATION	HOLDING TIME	SAMPLE VOL, mL(minimum)[b]
Nitroaromatics	G	Cool, 4°C, see footnote d. Store in the dark.	7 days to extract; 40 days to anal. after extraction.	1000 (1000)
Oil & Grease	G	Cool,4°C, adjust to pH<2 w/ HCL, H_2SO_4 or $NaHSO_4$	28 days	1000 (1000)
Radioactivity Alpha, Beta and radium		HNO_3 to pH <2	6 months	1 gallon
TOX (Total Organic Halides)	G-Amber	Cool, 4°C, H_2SO_4 to pH<2, see footnote d.	28 days	2 x 250 (2 x 100) fill with zero headspace
TOC	P,G	Cool, 4°C, adjust to pH<2 with HCL, H_2SO_4 or $NaHSO_4$	28 days	100 (25)

[a] P = Polyethylene container with polypropylene closure.
G = Glass container with Teflon-lined closure.
G-V = Glass VOA vial or bottle with Teflon septum.

[b] Desired volume. Minimum volume for analysis shown in ( ).

[c] Acidification inhibits microbial degradation of aromatic compounds such as benzene, toluene, and ethyl benzene. However, hydrochloric acid irreversibly degrades the purge-and-trap system. If aromatic compounds are anticipated at low levels and the sample is not expected to be analyzed immediately, acidify sample with 8 drops 6 N HCL or 6N H_2S0_4 per 40 mL VOA vial, or add 0.25 g of $NaHSO_4$ per 40 mL VOA vial.

[d] If residual chlorine is present, preserve with $Na_2S_2O_3$. Use 1 drop of 10% w/v $Na_2S_2O_3$ per 40 mL VOA vial or 0.8 mL of 10% w/v $Na_2S_2O_3$ per liter of water.

3.8 SAMPLE SHIPMENT.

3.8.1 Transportation.

The sample transportation options available to collectors are:

1) Collector delivery to the designated laboratory.

2) DTSC has a contract with Federal Express/ to deliver environmental and hazardous samples to the specified laboratory. Contact Ramona Pam of ECL for more information at (510) 540-3580.

3.8.2 Packaging.

Samples are packaged and labeled for two broad classes of samples:

1) Environmental Samples.
2) Hazardous Samples.

Water samples, background soil samples and air samples are usually considered to be environmental samples. Many soil and solid samples may also be environmental samples, depending on the site. As a general rule, samples are considered hazardous unless known to be otherwise. All samples from drums, tanks, and process streams are considered hazardous unless known to be non-hazardous.

Environmental samples have minimal special packaging and marking requirements. More information is given in Appendix C.

Packaging, labeling and marking requirements for shipping hazardous materials are much more extensive. Packages must comply with the Code of Federal Regulations, Title 49, Parts 171 through 179. Most samples will be classified as "limited quantities" under part 173.118 or part 173.153. Some shipments with very small samples may qualify "small quantities" in section 173.4. Specific instructions for use of these regulations are contained in Attachment C of this manual.

The 49 CFR regulations apply to surface and air shipments, although regulations for air shipments are more restrictive. All individual air carriers have additional requirements including the use of International Air Transport Association Dangerous Goods Regulations. For all practical purposes, these regulations have superseded 49 CFR for air shipments. Additional information can be obtained from individual air carriers.

ECL maintains a Federal Express account that can be used to ship hazardous samples. If DTSC field offices anticipate shipping samples by air, at least one person in each office should be familiar with shipping regulations.

3.9 DOCUMENTATION.

Field notes including boring logs and actual sampling procedures should be completely documented in accordance with SW-846 requirements. Chain of custody should be consistent with ECL Chain of Custody procedure and SW-846. These documents should be properly reviewed and compiled. This validation process should be documented with the appropriate signatures.

3.9.1 Chain of Custody.

Sample chain of custody (COC) refers to all records maintained in the field and laboratory for sample identification, transmittal and receipt. When a sample is maintained under chain of custody, the possession of the sample can be traced from collection until disposal. This procedure is necessary to insure that the sample or data derived from the sample is admissible as evidence in legal proceedings.

A sample is considered under custody if:

1) It is in your possession, or
2) It is in your view after being in your possession, or
3) It was in your possession and you locked it up, or
4) It is in a designated secure area.

In order to establish that a sample is valid, it is also necessary to document the measures taken to prevent or detect tampering or loss of sample. Measures must also be taken to detect and prevent tampering and contamination to sampling equipment and the sample site. This is done by the use of evidence tape, locks, custody seals and documented observations.

Since it is not always possible to know in advance if a sample will be used as evidence, all samples are maintained under chain of custody. Use of standard operating procedures throughout the sampling process will contribute to the consistency and quality of the data produced.

3.9.2 Sample Identification.

Preprinted sample collection labels similar to Figure 3.9-1 are recommended to identify samples collected for shipment to ECL. Labels for all collected samples including replicates, field blanks and spikes, should be filled out completely. The minimum information should be:

1) Site name & location
2) Field ID no.
3) Collection date and time
4) Collector name
5) Preservation

3.9.3 Custody Seals.

Custody seals are strips of printed tape that are used to demonstrate that no tampering has occurred. Seals can be placed over container caps, bags containing samples, or sample transport containers. They may also be used to seal sampling equipment or the site (e.g. house doors).

3.9.4 Chain of Custody Forms.

There are many COC transfers during the course of a sampling program. In order to document these transfers, all samples should be accompanied by the Sample Analysis Request (SAR) form (Fig. 4.0-3). A chain of custody section is included in the form. The original form always travels with the samples and the initiator keeps a copy. In some instances, such as the collection of air samples on solid sorbents, it is necessary to establish chain of custody procedures before samples are collected.

The custody records are used for a packaged lot of samples. More than one form may be used if the number of samples or the number of transfers exceeds the capacity of the form. The purpose is to document the transfer of a group of samples traveling together. When the packaged lot is broken down or regrouped, a new chain of custody form must be added.

To use COC forms, the following procedure should be used:

1) The originator fills in all requested information.

2) The person taking custody checks the sample label information against the custody records, and the condition of sample container and seals. Any discrepancies should be noted and reported

3) The originator signs on line 1 of the COC section and keeps the triplicate (pink) copy.

4) The person taking custody signs on line 2 and each person receiving custody

thereafter signs on lines 3, 4, 5, etc.

5) In all cases, inclusive dates should be clearly shown for each custody transfer.

6) The original (white) and duplicate (yellow) COC copies (SAR) are kept with the samples.

Samples should be delivered to the laboratory as soon as practicable. This is usually within 1 or 2 days of collection but may be sooner depending on the analyses required. The samples are relinquished to the Lab sample custodian, who will verify the COC information and take custody. A unique laboratory number will then be assigned to each sample as it is log to a permanent log book.

If a discrepancy appears between sample labels and the chain of custody records, the person receiving custody should attempt to resolve the problem by checking all available information and then document the situation on the custody form and in the project notebook. Changes should be noted in the remarks section and should be initialed and dated.

Transfers of sample(s), extracts or digestates should be documented also. The sample I. D., person's name, and inclusive dates should be clearly shown.

Sample Label

Collector: _____

Sample No.: _____

Place of Collection: _____

_____

Date Sampled: _____

Time Sampled: _____

Field Information: _____

_____

Lab # _____

Preservation: _____

_____

_____

Figure 3.9.1